

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
BEFORE THE  
BOARD OF PATENT APPEALS AND INTERFERENCES**

**APPLICANT:** West et al.  
**SERIAL NO.:** 10/074,219  
**FILED:** 12 February 2002  
**FOR:** Combination pH Electrode with Stable Standard Potential  
**EXAMINER:** Kaj K. Olsen  
**GROUP:** 1753  
**CONF. NO.:** 6185

Commissioner for Patents  
Board of Patent Appeals and Interferences  
P.O. Box 1450  
Alexandria, VA 22313-1450

**APPEAL BRIEF UNDER 37 C.F.R. §1.192**

**Introduction**

Appellant respectfully appeals the decision of Examiner Kaj K. Olsen dated April 26, 2006, finally rejecting claims 1 and 10-13, i.e., all of the claims still pending in the present application which have not been withdrawn from consideration. This appeal is directed to these claims.

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**(i) Real party in interest:**

The real party in interest in this appeal is Thermo Orion, Inc., the assignee of the subject application, which is a subsidiary of Thermo Electron Corporation.

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**(ii) Related appeals and interferences:**

Appellant hereby confirms that there are no related prior or pending appeals and/or interferences regarding this application. Likewise, there are no prior or pending related judicial proceedings.

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**(iii) Status of claims:**

Claims 1 and 10-13 are being appealed. The status of all claims filed in this application is as follows:

1. (Rejected) A combination glass pH electrode including a sensing electrode, a reference electrode possessing a standard potential, an outer tube having a liquid junction, an inner tube centrally located within the outer tube and connected to the outer tube by a top seal and a bottom seal, a reference electrolyte compartment located between the inner and outer tubes and the top and bottom seals having an opening in the outer tube, and reference electrolyte within the reference electrolyte compartment,

wherein the improvement comprises:

incorporation of a reference electrolyte compartment vent that minimizes moisture loss or pick-up from the surroundings yet under the influence of a partial vacuum created inside the reference electrolyte compartment, admits sufficient air to permit flow of added reference electrolyte through the liquid junction under the influence of gravity;

whereby the reference electrolyte is kept constant and the standard potential of the reference electrode is thereby stabilized;

whereby the combination glass pH electrode needs no calibration for up to two years.

2. (Withdrawn) An electrode as in Claim 1, where the noble metal in the

pH half-cell comprises platinum.

3. (Withdrawn) An electrode as in Claim 1, where the noble metal in the reference half-cell comprises platinum.

4. (Withdrawn) An electrode as in Claim 1, where the electrolyte in the pH half-cell comprises phosphate or borate buffer to stabilize the pH and a mixture of iodide and triiodide to stabilize the oxidation-reduction potential.

5. (Withdrawn) An electrode as in Claim 4, where the electrolyte in the pH half-cell has a pH slightly different from 7.00 in order to generate a potential across the pH bulb that cancels the potential across the liquid junction when the electrode is in pH 7.00 buffer so that the overall potential of the electrode is nearly zero.

6. (Withdrawn) An electrode as in Claim 5, where the electrolyte composition in the pH half-cell comprises 4 M KI, 0.0069 M KI<sub>3</sub>, 0.2 M H<sub>3</sub>BO<sub>3</sub>, adjusted to pH 7.05 with KOH.

7. (Withdrawn) An electrode as in Claim 1, where the electrolyte in the reference half-cell comprises phosphate or borate buffer and a mixture of iodide and triiodide to stabilize the oxidation-reduction potential.

8. (Withdrawn) An electrode as in Claim 7, where the electrolyte composition in the reference half-cell comprises 4 M KI, 0.0069 M KI<sub>3</sub>, 0.2 M H<sub>3</sub>BO<sub>3</sub>, adjusted to pH 7.05 with KOH.

9. (Withdrawn) An electrode as in Claim 1, where the porous, inert material

comprises porous ceramic.

10. (Rejected) An electrode as in Claim 1, where the opening to the reference electrolyte compartment is covered with an elastomeric septum closure that is perforated to permit insertion of a tube which by reason of its small inside diameter compared to its length serves to minimize diffusion of moisture into or out of the reference electrolyte compartment yet serves to admit sufficient air to allow electrolyte flow from the reference electrolyte compartment through the liquid junction under the influence of gravity.

11. (Rejected) An electrode as in Claim 10, further comprising a removable tube inserted into the perforation of the elastomeric septum closure, said tube having an inner diameter of about 0.5 mm and a length of about 10 mm, said tube being temporarily removed in order to replenish the reference electrolyte.

12. (Rejected) An electrode as in Claim 1, where the opening to the reference electrolyte compartment is covered with an elastomeric septum closure with a slit, said slit by reason of the substantial but not absolute barrier it provides between the reference electrolyte compartment and outside environment serving to minimize diffusion of moisture into or out of the reference electrolyte compartment yet serving to admit sufficient air to allow electrolyte flow from the reference electrolyte compartment through the liquid junction under the influence of gravity and at the same time serving to allow convenient replenishment of reference electrolyte by any liquid delivery means with delivery tip shaped so as to be able to pry open the slit, said slit then closing upon removal of delivery tip by reason of the restorative tendency of the elastomeric septum closure.

13. (Rejected) An electrode as in Claim 12, where the material of the septum closure comprises a silicone elastomer with a durometer of from about 30 to about 45.

14. (Withdrawn) An electrode as in Claim 1, where the storage sleeve seal between the sleeve and electrode may be effected in a manner not limited to the following: the sleeve is composed of an elastomeric material having a durometer between 75 and 80, and forms a seal with the electrode cap upon insertion of the electrode into the sleeve.

15. (Withdrawn) An electrode as in Claim 1, where the absorbent material in the storage sleeve comprises glass wool.

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**(iv) Status of amendments:**

Appellant has not filed any amendment subsequent to the Final Rejection issued on April 26, 2006.

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**(v) Summary of claimed subject matter:**

Claims 1 and 10-13 are on appeal herein. Claims 10-13 depend either directly or indirectly from claim 1.

An explanation of the invention defined in the claim 1 is provided in the specification as filed, particularly at page 6, lines 1-5, page 7, lines 1-4, page 9, lines 13-31, page 14, line 4 to page 15, line 9, page 18, lines 4-26, and also in Figures 1, 3, 4 and 6. Claim 1 relates generally to a combination glass pH electrode having a reference electrolyte compartment vent (element 2 in Figure 1 and element 21 in Figures 3 and 4) that is small enough to minimize diffusion of moisture into and out of the compartment, so that any change in the composition of the reference electrolyte over time by moisture loss or pick-up from the surroundings is minimized. By thus keeping the reference electrolyte constant, the standard potential of the reference electrode is stabilized. The stabilized standard potential advantageously provides a combination glass pH electrode which needs no calibration for up to two years. Yet the recited vent is not completely sealed, but under the influence of a partial vacuum created inside the reference electrolyte compartment by the flow of electrolyte out of the compartment through the liquid junction, admits sufficient air to permit flow of additional reference electrolyte through the liquid junction under the influence of gravity.

An explanation of the invention defined in claim 10 is provided in the specification as filed, particularly at page 8, lines 12-19 and in Figure 1. Claim 10 defines an embodiment of the invention wherein the reference electrolyte compartment vent comprises an elastomeric septum closure that is perforated to permit insertion of a tube of small inside diameter (element 2 in Figure 1), which functions to minimize diffusion of moisture and yet admits sufficient air to allow flow of reference electrolyte

through the liquid junction under gravity.

An explanation of the invention defined in claim 11 is provided in the specification as filed, particularly at page 14, lines 4-13 and in Figure 1. Claim 11 defines an embodiment of the invention wherein a removable tube (element 2 in Figure 1) having an inner diameter of about 0.5 mm and a length of about 10 mm is inserted into the perforation of the elastomeric septum closure, the tube being temporarily removed in order to replenish the reference electrolyte.

An explanation of the invention defined in claim 12 is provided in the specification as filed, particularly at page 8, lines 21-31 and page 14, lines 15-31, and in Figures 3 and 4. Claim 12 defines an embodiment of the invention wherein the reference electrolyte compartment vent comprises an elastomeric septum closure with a slit (element 21 in Figures 3 and 4), which functions to minimize diffusion of moisture into and out of the compartment, and yet admits sufficient air to allow flow of reference electrolyte through the liquid junction under gravity. The slit advantageously functions to allow convenient replenishment of reference electrolyte by any liquid delivery means with a tip shaped to pry open the slit, such as a needle, a pipet tip, or a bottle with a conically shaped tip. The slit will re-close after removal of the delivery tip.

An explanation of the invention defined in claim 13 is provided in the specification as filed, particularly from page 8, line 31 to page 9, line 2. Claim 13 defines an embodiment of the invention wherein the material of the elastomeric septum with a slit comprises silicone elastomer with a durometer of from about 30 to about 45.

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**(vi) Grounds of rejection to be reviewed on appeal:**

Four rejections have been maintained by the Examiner:

**Rejection No. 1:**

Claims 1 and 10-13 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

**Rejection No. 2:**

Claim 1 is rejected under 35 U.S.C. 102(b) as being anticipated by Frollini, Jr. et al. (USP 4,608,148).

**Rejection No. 3:**

Claim 1 in the alternative is rejected under 35 U.S.C. 103(a) as being unpatentable over Frollini, Jr. et al. (USP 4,608,148).

**Rejection No. 4:**

Claim 1 in the alternative is rejected under 35 U.S.C. 103(a) as being unpatentable over Frollini, Jr. et al. in view of Subsara et al. (USP 4,543,175) or Marsoner et al. (USP 5,160,420).

**(vii) Argument:**

**Rejection No. 1:**

**35 U.S.C. § 112, second paragraph, rejection:**

Claims 1 and 10-13 have been rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention. Reversal of this rejection is respectfully requested.

The following comments apply to each of the rejected claims, which are further argued individually below. Appellant respectfully submits that these claims are NOT to be considered as a group herein, and that each claim is patentable individually for the reasons set forth here and as set forth below. Accordingly, the following comments relate to each of the rejected claims, but are provided here once for the Board's consideration. Appellant further argues each claim separately, below. Accordingly, each claim must be considered on its own merits.

**General arguments against the Section 112, second paragraph, rejection of each of the claims:**

The functional language “minimizes moisture loss or pickup from the surroundings” recited in claim 1 and “minimize diffusion of moisture into or out of the reference electrolyte compartment” recited in claims 10 and 12, in combination with the functional language “admits sufficient air” recited in claims 1, 10 and 12, do serve to provide clear metes and bounds to distinguish the present invention over a prior art vent

structure. These terms define a range of air flow through the recited vent that would keep the reference electrolyte constant, stabilize the standard potential of the reference electrolyte, and provide a combination glass pH electrode which needs no calibration for up to two years, as recited in claim 1.

The Examiner objects to Appellant's use of the functional language "minimizes" to mean providing for a low level of moisture loss or pickup, instead of an absolute minimum which is obtained by a sealed vent, as confusing and unclear. However, one of ordinary skill in the art reading the claims as a whole would not be confused by the term "minimizes" because he would understand that "minimizes" does not refer to a sealed vent but to a very small open vent, because a vent that is sealed cannot "admit sufficient air to permit flow of added reference electrolyte through the liquid junction under the influence of gravity." The skilled artisan should be able to at least empirically determine a range of vent sizes that falls within the "minimizes" and "admits sufficient air" limitations, and also meets the "whereby the combination glass pH electrode needs no calibration for up to two years" limitation. Therefore, "minimizes" and "admits sufficient air" can be clearly construed by the skilled artisan as defining the range of vent sizes that provide a combination glass pH electrode which "needs no calibration for up to two years."

At page 8 of the Final Office Action, the Examiner argues that the concept of when calibration is needed is not definite, but entirely relative. Appellant does not understand the Examiner's reasoning:

"If one doesn't use the electrode for an extended period of time, one doesn't "need" any calibration."

But a pH electrode is a tool meant to be used. A combination glass pH electrode of the prior art that has not been used for an extended period of time would still need calibration immediately before it is used again, regardless of the length of time it has remained unused. In contrast, if Appellant's inventive pH electrode is left unused for a period of time up to two years, it would not need calibration before it is used again. The Examiner also asserts:

“If one doesn't desire a high accuracy, then one also doesn't “need” very frequent calibration.”

If the skilled artisan does not require a high degree of accuracy, he would use a cheaper and easier method for measuring pH, such as pH paper. The skilled artisan would not waste an expensive piece of lab equipment, such as a pH electrode, on rough pH measurements. Only if the skilled artisan desires a high degree of accuracy would he use a pH electrode as a measuring tool. In order to maintain a high degree of accuracy, the pH electrodes of the prior art need to be calibrated frequently, certainly more frequently than once every two years. Page 18, third paragraph of the specification discloses that a standard pH electrode without the vent of invention has a drift of about 1.2 pH units a year if it is not calibrated (see also Figure 7). This error is unacceptable and would require calibration more frequently than once a year, because the required accuracy for many, if not most, pH measurements is about 0.1 pH units (specification, page 18, second paragraph). In contrast, the pH electrode of invention incorporating the recited vent is shown to have a pH drift of about 0.02 pH units per year, and maximally about 0.07 pH units over two years (specification, page 18, second paragraph, see also Figure 6). This is within the usual 0.1 pH unit accuracy requirement, so the pH electrode of invention does not need calibration for up to two years.



The Examiner is admittedly unaware of any industrial standard for calibration of combination pH electrodes. Appellant respectfully submits excerpts from Thermo Orion's 2001 product catalog as evidence of standard calibration frequency in the art before the filing date of the present application (included in the Evidence Appendix). At the bottom of page 59, the catalog instructs the pH electrode user:

"Calibration verifies [pH] electrode slope and proper function. **At least once a day**, calibrate with two or three buffers or standards that bracket the expected sample range." (Emphasis added.)

Appellant also submits a Walchem pH electrode user manual dated November 2004 and a Digital Analysis Corp. webpage printout on pH probe maintenance (both included in the Evidence Appendix) as evidence of current standard calibration frequency for pH electrodes that do not incorporate the vent of present invention. At page 10 under the title "Frequency of Calibration," the Walchem user manual instructs the pH electrode user:

"Although the frequency of calibration is solely the responsibility of the user, **once a week** is the longest recommended interval between calibrations." (Emphasis added.)

At page 2 of the webpage printout, Digital Analysis Corp. instructs the pH electrode user:

"pH Probes will normally require weekly or monthly cleanings and **monthly calibrations**. The actual frequency is a function of the installation environment but could be as often as a **couple of times a day**." (Emphasis

added.)

So from the above evidence, one can see that industrial standards for calibration frequency of combination pH electrodes that do not incorporate the vent of present invention run from a couple of times a day to once a month. This frequency remains the industrial standard even after the filing date of Appellant's patent application up to the present. Thus, Appellant's inventive combination glass pH electrode which needs no calibration for up to two years is a significant contribution over the industrial standard, which requires at least monthly calibrations.

For at least the above reasons, claims 1 and 10-13 do particularly point out and distinctly claim the subject matter which Appellant regards as the invention. Accordingly, the 35 U.S.C. § 112, second paragraph rejection should be reversed.

#### **Specific Individual Claim Arguments:**

##### **Claim 1:**

As set forth above, the vent limitation "minimizes moisture loss or pick-up from the surroundings yet under the influence of a partial vacuum created inside the reference electrolyte compartment, admits sufficient air" is clearly defined by the further limitation "whereby the combination glass pH electrode needs no calibration for up to two years." Accordingly, the § 112, second paragraph rejection should be reversed. Such action is respectfully requested.

##### **Claim 10:**

This dependent claim further defines the structure of vent of claim 1 as the opening to the reference electrolyte compartment covered with an elastomeric septum closure that is perforated to permit insertion of a tube which serves to “minimize diffusion” and yet “admit sufficient air.” The functional limitations “minimize diffusion” and “admit sufficient air” are clearly defined by the limitation of claim 1 “whereby the combination glass pH electrode needs no calibration for up to two years.” As set forth above, the need for calibration is not completely relative, but is defined by industry standards and usual accuracy requirements. Accordingly, the § 112, second paragraph rejection should be reversed. Such action is respectfully requested.

**Claim 11:**

This dependent claim further defines the vent of claims 1 and 10 as comprising a removable tube with the recited dimensions inserted into the perforation of the elastomeric septum closure. Claim 11 clearly defines the structure that serves to “minimize diffusion,” “admit sufficient air,” and provide a pH electrode that “needs no calibration for up to two years” as the tube having an inner diameter of about 0.5 mm and a length of about 10 mm which is inserted into the perforation of the elastomeric septum closure that covers the opening in the reference electrolyte compartment. Accordingly, the § 112, second paragraph rejection should be reversed. Such action is respectfully requested.

**Claim 12:**

This dependent claim further defines the structure of the vent of claim 1 as the opening to the reference electrolyte compartment covered with an elastomeric septum closure with a slit, which provides a substantial but not absolute barrier between the

reference electrolyte compartment and the outside environment, and so serves to “minimize diffusion” and yet “admit sufficient air.” The functional limitations “minimize diffusion” and “admit sufficient air” are clearly defined by the limitation of claim 1 “whereby the combination glass pH electrode needs no calibration for up to two years.” As set forth above, the need for calibration is not completely relative, but is defined by industry standards and usual accuracy requirements. Accordingly, the § 112, second paragraph rejection should be reversed. Such action is respectfully requested.

**Claim 13:**

This dependent claim further defines the structure of the vent of claims 1 and 12 where the material of the septum closure comprises a silicone elastomer with a durometer of from about 30 to about 45. Claim 13 clearly defines the structure that serves to “minimize diffusion,” “admit sufficient air,” and provide a pH electrode that “needs no calibration for up to two years.” Again, the functional limitations “minimize diffusion” and “admit sufficient air” are clearly defined by the limitation of claim 1 “whereby the combination glass pH electrode needs no calibration for up to two years.” As set forth above, the need for calibration is not completely relative, but is defined by industry standards and usual accuracy requirements. Accordingly, the § 112, second paragraph rejection should be reversed. Such action is respectfully requested.

For the foregoing reasons, Appellant respectfully submits that reversal of the § 112, second paragraph rejection of claims 1 and 10-13 is proper.

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**Rejection No. 2:**

**35 U.S.C. § 102(b) rejection:**

Claim 1 has been rejected under 35 U.S.C. § 102(b) as being anticipated by Frollini, Jr. et al. (USP 4,608,148) (hereinafter “Frollini”). Reversal of this rejection is respectfully requested.

**Arguments against the Section 102(b) rejection claim 1:**

Anticipation requires identity of invention. Frollini fails to anticipate claim 1 because Frollini neither teaches nor suggests the pH electrode of invention comprising a reference electrolyte compartment vent that minimizes moisture loss or pick-up from the surroundings, yet under the influence of a partial vacuum created inside the reference electrolyte compartment, admits sufficient air to permit flow of added reference electrolyte through the liquid junction under the influence of gravity; whereby the reference electrolyte is kept constant and the standard potential of the reference electrode is thereby stabilized; whereby the combination glass pH electrode needs no calibration for up to two years.

The Examiner points to the opening 50 of unspecified dimensions in the outer

tube shown in Figure 1 of Frollini as the structure that meets the language of claim 1, asserting that the limitation “needs no calibration for up to two years” is unclear, indefinite, and relative. However, as set forth above, industrial standards do exist for calibration frequency of prior art combination pH electrodes that do not incorporate the vent of present invention, running from a couple of times a day to at least once a month. Thus the limitation “needs no calibration for up to two years” clearly defines a contribution over the prior art. Accordingly, the terms “minimizes” and “admits sufficient air” can be clearly construed by the skilled artisan as defining the range of vent sizes that provide a combination glass pH electrode which “needs no calibration for up to two years.”

The pH electrode of Frollini is one of the prior art structures for which the present invention is a contribution over. The large opening 50 in Figure 1 of Frollini corresponds to the opening (17) in Figures 1, 3, and 4 of the specification and the “opening in the outer tube” as recited in the preamble of claim 1. The large opening 50 in the pH electrode of Frollini is the type found in prior art pH electrodes that produce the large standard potential drift shown in Figure 7 and described at page 18, third paragraph, of the specification. Because these prior art pH electrodes exhibit a large standard potential drift of about 1.2 pH units per year (page 18, third paragraph), one of skill in the art would find it necessary to calibrate these prior art pH electrodes more often than once a year, and certainly more often than every two years, to obtain reasonably accurate measurements within about 0.1 pH units (see page 18, second paragraph). The present invention, two embodiments of which are shown in Figures 1, 3, and 4 of the present application, significantly decreases the size of opening (17) (corresponding to Frollini’s opening 50) in order to minimize moisture loss and pick-up from the surroundings and yet admit sufficient air, so that the pH electrode needs no calibration for up to two years. Frollini certainly does not teach or suggest a pH electrode that needs no calibration for up

to two years. Frollini does not even mention calibration frequency. The pH electrode taught by Frollini is of the type that is shown in the present application to exhibit a large standard potential drift. The skilled artisan would find that for normal operation, the pH electrode of Frollini needs calibration according to industry standards, at the very least once a month.

For the above reasons, Frollini fails to teach or suggest each and every limitation of claim 1, so Frollini fails to anticipate claim 1. Accordingly, the 35 U.S.C. § 102(b) rejection should be reversed.

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**Rejection No. 3:**

**35 U.S.C. § 103(a) rejection:**

Claim 1 has been rejected in the alternative under 35 U.S.C. § 103(a) as being unpatentable over Frollini. This is a new rejection that has not been presented in previous Office Actions. Nevertheless, Appellant is presenting arguments below against this new rejection. Reversal of the rejection is respectfully requested.

**Arguments against the Section 103(a) rejection of claim 1:**

Frollini fails to teach or suggest each and every limitation of claim 1 for the reasons presented in arguments above against the 35 U.S.C. § 102(b) rejection over Frollini. Applicant has defined “minimizes,” “admits sufficient air,” and “needs no calibration for up to two years” with sufficient specificity to read free of the teachings of Frollini. Contrary to the Examiner’s opinion, Figures 2 and 3 of Frollini do not teach or suggest that the liquid junction (136 or 236) can be located on the outer tube. Figures 2 and 3 of Frollini appear to show sealing between the inner tube and the outer tube, though no details are given about these seals. The liquid junctions 136 and 236 are



roughly depicted at the edges of the outer tubes and the bottom seals. Frollini, by clearly depicting liquid junction **36** located on bottom seal **52** in Figure 1, suggests to the skilled artisan that the liquid junctions **136** and **236** are analogously located on bottom seals in Figures 2 and 3. In addition, Frollini explicitly states at col. 4, lines 60-65 and at col. 5, lines 8-13 that elements **136** and **236** indicate elements identical or substantially identical to the corresponding element **36** in Figure 1. Thus, Frollini suggests that liquid junctions **136** and **236** are located in bottom seals in an identical manner as liquid junction **36**. Frollini provides no suggestion or motivation to modify liquid junction **36** of Figure 1 from being on the bottom seal to being on the outer tube. The Examiner is using impermissible hindsight reconstruction based on Appellant's disclosure to modify the teaching of Frollini to move the position of liquid junction from the bottom seal as taught to the outer tube, as recited in claim 1.

For the above reasons, Frollini fails to teach or suggest each and every limitation of claim 1, and also fails to provide motivation to modify its teachings, so Frollini fails to render claim 1 obvious. Accordingly, the 35 U.S.C. § 103(a) rejection should be reversed.

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**Rejection No. 4:**

**35 U.S.C. § 103(a) rejection:**

Claim 1 has been rejected in the alternative under 35 U.S.C. § 103(a) as being unpatentable over Frollini in view of Subsara et al. (USP 4,543,175) (hereinafter “Subsara”) or Marsoner et al. (USP 5,160,420) (hereinafter “Marsoner”). Reversal of the rejection is respectfully requested.

**Arguments against the Section 103(a) rejection of claim 1:**

As presented in arguments above, Frollini fails anticipate or render obvious claim 1. The opening **50** of Frollini is not capable of minimizing moisture loss or pick-up yet admitting sufficient air so that the combination glass pH electrode needs no calibration for up to two years. Subara and Marsoner both fail to remedy the deficiencies of Frollini.

It would not be obvious to combine refill sleeve **20** of Subsara with the pH electrode of Frollini to arrive at the invention of claim 1, for the following reasons. The

Examiner relies on Subsara to provide motivation to combine refill sleeve **20** with the pH electrode of Frollini, so that opening **50** of the pH electrode can be sealed so as to prevent electrolyte loss when the electrode is not being operated. But a sealed pH electrode is not Appellant's claimed invention. The pH electrode of claim 1 incorporates "a reference electrolyte compartment vent that minimizes moisture loss or pick-up from the surroundings yet under the influence of a partial vacuum created inside the reference electrolyte compartment, admits sufficient air to permit flow of added reference electrolyte through the liquid junction under the influence of gravity." The Examiner admits that Subsara fails to teach or suggest using the sleeve as a partial obscurant of the refill opening, but asserts that the sleeve is capable of partially obscuring the opening until it met the claim limitations, and so claim 1 is obvious. This is a case of impermissible hindsight reconstruction, since Subsara fails to provide motivation to modify its sealed opening to a partially obscured opening. Even if one of ordinary skill in the art were motivated to combine Subsara with Frollini, neither reference provides teaching, suggestion, or motivation to permanently partially obscure the opening in the reference electrolyte compartment. Even if the sleeve of Subsara is capable of partially obscuring the opening to meet the claim limitations, the skilled artisan would not do so without motivation, so the pH electrode with the vent of invention is not obvious over the combination of Subsara and Frollini.

It would not be obvious to combine the automatic reference electrolyte refill system of Marsoner with the pH electrode of Frollini to arrive at the invention of claim 1, for the following reasons. The Examiner relies on Marsoner to provide motivation to combine sealed tubes **21** and **22** with the pH electrode of Frollini, so that reference electrolyte can be automatically delivered and undesirable mixing of sample and electrolyte can be avoided. However, Appellant does not claim or disclose automatic delivery of reference electrolyte. Nor is undesirable mixing of sample and electrolyte

prevented by sealed tubes **21** and **22** in Marsoner. On the contrary, undesirable mixing of sample and electrolyte is prevented by capillary tube **53**, as disclosed by Marsoner at col. 6, lines 3-14 (below).

“Since the interior of the reference electrode is subject to a lower hydrostatic pressure during the process of measurement because of the lower position of the KCl storage tank **28**, sample liquid may enter the reference electrode via the diaphragm **51**. It will flow into the capillary tube **53** immediately behind the diaphragm **51**, and an undesirable mixing of the electrolyte and the sample liquid is thus avoided. The sample liquid which has entered the reference electrode will leave again during the cleaning cycle, during which a partial vacuum is established in the measuring channel, and may be rinsed off.”

Therefore, Marsoner fails to provide motivation to combine sealed tubes **21** and **22** with the pH electrode of Frollini to arrive at the claimed invention.

Even if Marsoner did provide motivation to combine, the combination of Marsoner with Frollini fails to teach or suggest each and every claim limitation. As the above quotation shows, Marsoner does not teach or suggest the claim limitation “yet under the influence of a partial vacuum created inside the reference electrolyte compartment, admits sufficient air to permit flow of added reference electrolyte through the liquid junction under the influence of gravity.” Instead of reference electrolyte flowing through the liquid junction as recited, Marsoner discloses that under the influence of lower hydrostatic pressure inside the reference electrode, sample liquid flows into the reference electrode. In addition, Marsoner discloses at col. 6, lines 15-16 that “the reference electrode **50** represents a closed system.” Therefore, the sealed tubes

**21** and **22** of Marsoner cannot “admit sufficient air,” as recited in claim 1. Since the system of Marsoner cannot “admit sufficient air to permit flow of added reference electrolyte through the liquid junction under the influence of gravity,” reference electrolyte must be forced through the fine-pored diaphragm **51** (col. 5, line 65 to col. 6, line 3), “This [reference] electrode is closed off by a fine-pored diaphragm **51**, through which a small dose of [reference electrolyte] KCl may be forced at the beginning of each measurement or pH calibration.” So Marsoner also fails to disclose flow of reference electrolyte through the liquid junction under the influence of gravity, as recited in claim 1. Finally, Marsoner fails to teach or suggest that sealed tubes **21** and **22** are able to stabilize the standard potential of the reference electrode and provide a combination glass pH electrode that needs no calibration for up to two years.

For the foregoing reasons, the cited references fail to provide motivation to combine teachings, and even if they did provide motivation, the combination of teachings fails to teach or suggest each and every limitation of claim 1. The Examiner is using impermissible hindsight reconstruction based on Appellant’s disclosure to modify the pH electrode of Frollini with sealed tubes **21** and **22** of Marsoner, or with the refill sleeve **20** of Subsara. Accordingly, the 35 U.S.C. § 103(a) rejection of claim 1 over Frollini in view of Marsoner or Subsara should be reversed.

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**Conclusion:**

For the reasons set forth above, Appellant respectfully requests that the Board reverse the Examiner in this application.

**TIME EXTENSION REQUEST**

Appellant respectfully requests a two-month extension of time for the filing of this brief. The original submission deadline was 26 September 2006. This filing is being made on or before November 26, 2006.

**FEE AUTHORIZATION**

Please charge all fees due in connection with this filing to our Deposit Account – No. 19-0733.

Respectfully submitted,

Appeal Brief  
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Date: 21 November 2006

**(viii) Claims appendix:**

The following is an appendix containing a copy of the claims involved in the appeal (double spaced).

1. A combination glass pH electrode including a sensing electrode, a reference electrode possessing a standard potential, an outer tube having a liquid junction, an inner tube centrally located within the outer tube and connected to the outer tube by a top seal and a bottom seal, a reference electrolyte compartment located between the inner and outer tubes and the top and bottom seals having an opening in the outer tube, and reference electrolyte within the reference electrolyte compartment,

wherein the improvement comprises:

incorporation of a reference electrolyte compartment vent that minimizes moisture loss or pick-up from the surroundings yet under the influence of a partial vacuum created inside the reference electrolyte compartment, admits sufficient air to permit flow of added reference electrolyte through the liquid junction under the influence of gravity;

whereby the reference electrolyte is kept constant and the standard potential of the



reference electrode is thereby stabilized;

whereby the combination glass pH electrode needs no calibration for up to two years.

10. An electrode as in Claim 1, where the opening to the reference electrolyte compartment is covered with an elastomeric septum closure that is perforated to permit insertion of a tube which by reason of its small inside diameter compared to its length serves to minimize diffusion of moisture into or out of the reference electrolyte compartment yet serves to admit sufficient air to allow electrolyte flow from the reference electrolyte compartment through the liquid junction under the influence of gravity.

11. An electrode as in Claim 10, further comprising a removable tube inserted into the perforation of the elastomeric septum closure, said tube having an inner diameter of about 0.5 mm and a length of about 10 mm, said tube being temporarily removed in order to replenish the reference electrolyte.

12. An electrode as in Claim 1, where the opening to the reference electrolyte compartment is covered with an elastomeric septum closure with a slit, said slit by reason of the substantial but not absolute barrier it provides between the reference electrolyte compartment and outside environment serving to minimize diffusion of moisture into or

out of the reference electrolyte compartment yet serving to admit sufficient air to allow electrolyte flow from the reference electrolyte compartment through the liquid junction under the influence of gravity and at the same time serving to allow convenient replenishment of reference electrolyte by any liquid delivery means with delivery tip shaped so as to be able to pry open the slit, said slit then closing upon removal of delivery tip by reason of the restorative tendency of the elastomeric septum closure.

13. An electrode as in Claim 12, where the material of the septum closure comprises a silicone elastomer with a durometer of from about 30 to about 45.

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**(ix) Evidence appendix:**

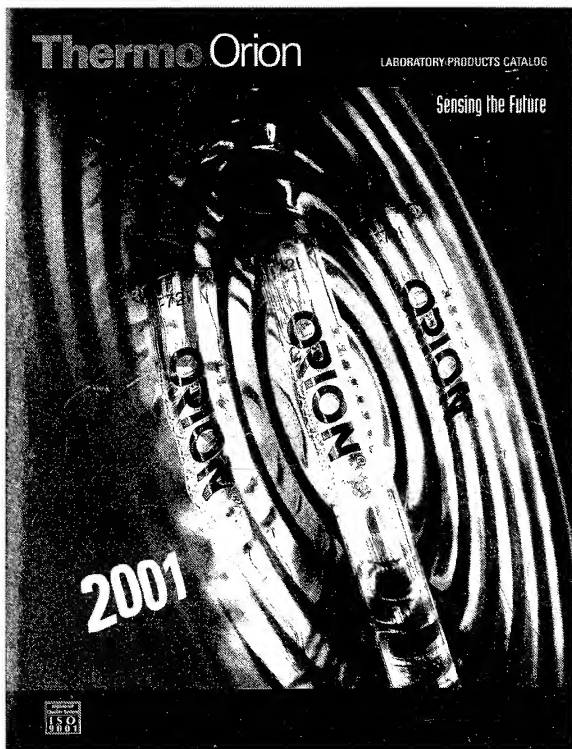
Appellant believes that the prior art cited by the Examiner in support of the rejections need not be attached here, as these documents are already part of the record in this appeal.

Appellant respectfully submits herewith excerpts from Thermo Orion's 2001 product catalog (pages 34-38) as evidence of the industrial standard for calibration frequency of pH electrodes known in the art before the filing date of the present application.

Appellant respectfully submits herewith a Walchem pH electrode user manual dated November 2004 (pages 39-50), and a Digital Analysis Corp. webpage printout on pH probe maintenance (pages 51-54) as evidence of the current industrial standard for calibration frequency of pH electrodes that do not incorporate the vent of present invention.

At page 8 of the Response to Office Action filed February 14, 2006, Appellant distinguishes the claimed pH electrode over the pH electrode of the prior art, because the claimed pH electrode provides a stabilized reference potential (as evidenced by Figure 6 compared to Figure 7 of the specification as filed) so that the claimed pH electrode does not need calibration for up to two years, whereas the prior art pH electrode requires calibration more often than every two years. At page 8 of the Final Office Action dated April 26, 2006, the Examiner admits lack of knowledge of any industrial standard for calibration of pH electrodes, and so presumes that needing no calibration for up to two years is not a definite limitation. Appellant herein submits supplemental evidence of the industry standard for frequency of calibration of the prior art pH electrode, ranging from

more than once a day to at least once a month.



## pH, ORP and ISE Theory

### Choosing the Correct Reference System

Three criteria apply when you choose a reference electrode:

- The reference electrode should provide a stable and reproducible potential under a wide variety of sample conditions.
- The reference electrode filling solution should not interfere with the sensing electrode. Ions that interfere with the analysis should not be introduced into the sample by the reference electrode.
- The filling solution should flow freely with no leaking or plugging of the junction by the sample.

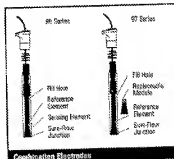
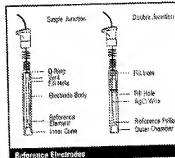
### Reference Electrode for Half-Cell Systems

Half-cell reference electrodes help complete the measuring circuit when using a half-cell sensing electrode. Often recommended two types of reference electrodes, both include the silver-silver chloride reference junction. The Sure-Flow Junction provides many benefits, including working in dirty or viscous samples without clogging. The Sure-Flow reference is a single junction type which uses a filling solution saturated with silver (in the form of silver chloride) to verify the replacement of the internal cell. The double junction type is useful when the filling solution of a single junction electrode contains an ion that interferes or reacts with the ion being analyzed. For example, use of potassium chloride fill solution is undesirable for a chloride analysis because the fill solution introduces more chloride into the sample and leads to falsely high results. The double junction electrode allows for selection of a non-interfering solution to measure the sample. In the case of chloride analysis, potassium nitrate, which causes no interference, may be used as a filling solution. Double junction electrodes also allow some additional fill solution choices when analyzing unusual samples that could cause changes in liquid junction potentials.

### Combination Reference Electrode Systems

Half-cell systems use all purpose reference systems, which may not provide the needed performance under some application conditions. With combination electrodes, the built-in reference system meets all of the criteria for a reference electrode. Often combination electrode designs provide an equilibrium reference system for the specific ion of interest. In the case of pH electrodes, combination electrode designs allow for unique electrode constructions for measuring flat surfaces, small samples in test tubes or placing acid samples and septa. Orion Sure-Flow junction design, on many pH and ISE combination electrodes, improves electrode performance because the sleeve construction allows a unique flow rate of reference filling solution into the sample. The uniform flow rate produces stable reference potentials for faster response and better stability. In addition, the electrodes are cleaned by simply opening the reference junction.

The latest Orion reference system is found in the Aquaflo electrode line which is a high performance polymer jacketed the Ag wire from the sample. These patented double junction, low maintenance electrode systems offer fast response due to an open junction. They are an ideal replacement for reference electrodes as they do not contain mercury and the isolated reference allows them to be used with biological applications. Aquaflo electrodes also offer excellent performance in dirty samples.



Salt	Concentration	Use
Ag <sub>2</sub>	Saturated or 4 M	Generally useful as a source of Ag <sup>+</sup> ions. Do not use in absence of ligand
NH <sub>4</sub> <sup>+</sup> , P <sup>+</sup> , Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup>	Good precipitants/complexing agents	Generally useful. Lower solubility products than saturated KNO <sub>3</sub> in dilute (0.1 M) NaCl. Ionic strength complexing. Above 0.5 M ionic strength KNO <sub>3</sub> or potassium acetate
KNO <sub>3</sub>	Saturated	Best Cl <sup>-</sup> precipitant

Orion pH electrodes are constructed with a variety of reference junctions, such as ceramic, vitreous, glass or Sure-Flow<sup>®</sup>. Based on the material of the electrode and intended application, a pH electrode whose junction material is compatible with the sample should be used. For most clean, aqueous samples, any junction type is acceptable. However when measuring dirty slurries, the Sure-Flow junction is always recommended. Refer to pages 23, 63 and 84 for more information on choosing a pH electrode with an appropriate reference junction. Most Orion ISE combination electrode systems and half-cell systems employ the Sure-Flow junction for measurements in any sample type.

A liquid junction potential develops at the reference electrode junction where the sample and filling solutions mix. Changes in liquid junction potentials can cause errors during electrode determinations. The filling solution potential should be defined for accurate measurements. In most pH measurements standard buffer junction potentials are not noticeable. However, in other applications such as ion-selective electrodes, acceptable differences are made to ±2% accuracy. This situation could be altered by a typical solid-state junction potential determination between the sample and standard of 0.1 M NaCl. Junction potentials arise when ions in solution move at different rates. The cations, for example, will move more slowly than the anions. Consequently, anion leaves faster leading to build up charge that is added to the reference potential. Since the charge is not due to the ion of interest, a measurement error occurs. Mechanically, an event bordering a sample from another solution is necessary to have a small concentration of reference filling solution. The filling solution must be able to flow through the junction. The electrolyte that best satisfies the above requirement is one that uses a silver-silver chloride salt in the Orion Dura-Cell junction. This reference ensures continuous flow as long as the analyte is carefully maintained at a higher level of filling solution as the reference electrode compared to its internal level. The reference electrode allows the method advantage of what it can be easily filled to zero.

SIGNIFICANCE

The most important variable the analyst can control is the composition of the reference filling solution. If the analyst has the Orion Snow-Flow *direct injection reference electrode*, the optimum solution for each particular application may be selected. Optimum Results<sup>®</sup> application solutions offer another aspect of control for the analyst. These reference filling solutions are used with Orion's keypad<sup>®</sup> construction kits. Each control solution formulation is designed to provide a narrow range potential for the particular application (patent pending). By reducing the effects of sample temperature changes, Optimum Results solutions enhance the electrode stability and response time to improve measurement accuracy.

## pH, ORP and ISE Theory

### For Best Results Use Good Laboratory Practices

Follow the recommendations below for accurate pH and ISE measurements. pH and ISE electrodes are sensitive measuring devices and should be cared for properly.

#### Proper Electrode Storage

Proper electrode storage maximizes electrode performance and extends the electrode life. For storage information see page 66 (pH electrodes) and pages 77 and 78 (ISE electrodes). Caution: do not store the electrodes in distilled water. The filling solution will be diluted and the electrode response will be slow.

#### Proper Maintenance and Cleaning

Inspect the electrode weekly for scratches, cracks or salt crystallization. If the readings become slow or drift, clean the electrode per the manufacturer's instructions. Excessive cleaning may impair electrode performance and shorten electrode life.

#### Electrode Fill Hole Cover

If using a refillable electrode, remove fill hole covers during calibration and measurement to ensure a uniform flow of electrode filling solution. Cover the fill hole overnight and during storage.

#### Filling Solution Level

The filling solution level must be higher than the sample level to maintain a uniform flow of filling solution. At least 1 inch above sample height is recommended.

#### Rinsing

Rinsing prevents contamination by carry-over on the electrodes. Rinse with deionized water or an aliquot of the buffer, standard or sample. Caution: do not wipe the pH electrode glass bulb. Transfer of static charge onto the glass bulb will result in slow or drift response. To avoid damage and contamination do not wipe the ISE liquid membrane surface.

#### Stirring

Stir all buffers, standards and samples at a uniform rate to obtain a representative sample measurement and improve electrode response time. Use a magnetic stirrer at a medium speed, use a piece of insulating material (e.g., teflon) or cardboard between the stir plate and the beaker to prevent heat transfer.

#### pH Buffers and ISE Standards

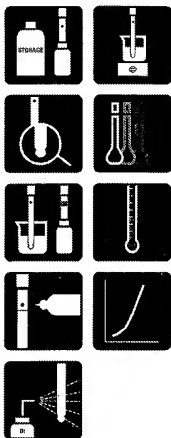
pH buffers and ISE standards should be accurate and free of contamination. Keep the buffer or standard bottles tightly sealed. Do not re-use buffers and standards. Verify the buffer or standard is within the electrode's range before use. If trouble arises, always use fresh buffers or standards. Use volumetric glassware to prepare solutions accurately.

#### Temperature

To account for pH slope, buffer and sample changes, use a separate or integrated automatic temperature compensation (ATC) or digital Light™ temperature compensation on Orion Perstat™ pH meters. For ISE electrodes, calibration and measurement should be performed at the same temperature.

#### Calibration

Calibration verifies electrode slope and percent function. At least once a day, calibrate when you use three buffers or standards that bracket the expected sample range. Choose pH buffers that are no more than three pH units or no less than one pH unit apart. ISE standards should differ in concentration by a factor of ten.





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1-616-594X-ION, X<sup>2</sup>, AT in One, Aqua, AssuredAccuracy, AUTO-BAR, AUTOCAL, AUTO DISPENSER, AUTO-LOD, AUTO-STIR, AUTO-READ, BOD EZ, Cable-Free, CERTI-CAL, CISA, DissOLLECT, DropPLUS, Digital Loop, Electrical, ShareProbe, Extra EasyPoint Value, FAST OK, Flash EZ, IAP, GLPac, GLPcheck, GLPcheck, IANalyzer, KAT, LABConnect, Loop, Minimum Str Requirement, MSR, RDS, One-Touch, One-Touch Calibration, One-Touch Measurement, Optimum Results, pHcheck, pHcheck MMS, pHcheck PortProbe, pHcheck Quatrode, pHcheck Titrator, Pure Water, Quikcheck, rLink, RDS, RDS Resonator, Sage, SAGB, Stacked, Stat Foc, The Enhanced Lab, ThermoSense, Titrator, TRL-Map, Undersat pH, Universal Access and Wine Master are trademarks of Orion Research, Inc.

Guaranteed Success and The Technical Edge are service marks of Orion Research, Inc.

PeriFECT meters are protected by U.S. patent 4,321,544. Other patents pending.

RDS and PeriFECT RDS are protected by U.S. patent 4,495,050. Other patents pending.

ORION Series A meters and 900A meter are protected by U.S. patents 5,106,578, 5,198,082, 5,334,209 and 5,345,753.

ORION R1, R2, R1, and R2 series glass electrodes are protected by U.S. patents 4,661,236 and 4,687,840.

Sure-Flow electrodes are protected by European Patent 278,579 and Canadian Patent 1,286,735. Other patents pending.

Ionplus electrodes and Optimum Results solutions have patents pending.

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The specifications, descriptions, drawings, ordering information and part numbers within this document are subject to change without notice.

This publication supersedes all previous publications on this subject.

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# W A L C H E M

## WALCHEM WEL Series pH/ORP ELECTRODES

### 1.0 Operation

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The number of parts required and the installation will vary with the model ordered. The electrode consists of a replaceable pH or ORP electrode cartridge, an electrode housing which may also contain a temperature compensation element and/or a reliable differential-type preamplifier with solution ground, and a mounting nut and adapter for in-line mounted models.

#### Electrode Cartridges:

There are three pH electrode cartridge choices. Each is best suited for specific applications:

WEL-PHF-NN is a flat surface glass pH electrode which will function well in almost any application, and will perform especially well if the solution tends to coat an electrode with solids or oils.

WEL-PHB-NN is a bulb-type glass pH electrode which will function well in clean chemical applications.

WEL-PHH-NN is a flat surface glass pH electrode which is highly resistant to attack by acidic fluoride solutions that would quickly etch the glass of a standard pH electrode.

There is one choice of ORP electrode cartridge. The WEL-MVF-NN is a flat surface platinum electrode which will work in almost any application.

#### Electrode Housings:

There are six housings available, which are selected based upon the type of electrode cartridge used, and the type of instrument to be connected:

The 102581 housing contains a Pt1000 automatic temperature compensation (ATC) element and differential preamplifier with solution ground. This housing is specified in pH applications when the error due to changing temperature is significant to your process (see table below), and the instrument that the electrode will connect to either does not have an integral preamplifier (such as the WPH or WNI series) or if the distance between the instrument and the electrode will exceed 20-30 feet. It should not be specified for ORP applications, since no ATC is used. It is supplied with a 20 ft. cable with tinned leads.

The 102758 housing is identical to the 102581 housing except it uses a Pt100 ATC element.

The 102606 housing contains only the differential preamplifier with solution ground, and does NOT contain the Pt1000 ATC element. This housing is specified when the error due to temperature is insignificant to your process, and the instrument you will attach does not have a preamplifier in it (such as the WPH or WNI series), or is more than 20-30 feet away. It would also be used with an ORP cartridge, since there is no ATC used in ORP applications. It is supplied with a 20 ft. cable with tinned leads.

The 102582 housing contains only the Pt1000 ATC element with solution ground, but does NOT contain the preamplifier. This is used in pH applications where the error due to temperature is significant to your process, and the instrument to be attached contains an integral preamplifier (such as the W-250/260 or W-130/230 series), and will be located within 20-30 feet of the electrode. It should not be used in ORP applications. It is supplied with a 20 ft. cable with a BNC connector for the pH signal and tinned leads for the ATC and solution ground signals.

The 102759 housing is identical to the 102582 housing except it uses a Pt100 ATC element.

The 102607 housing contains neither an ATC element, nor the preamplifier. It should be used in pH or ORP applications where the error due to temperature is insignificant to your process, and the instrument to be attached contains an integral preamplifier (such as the W-250/260 or W-130/230 series), and will be located within 20-30 feet of the electrode. It is supplied with a 20 ft. coax cable with a BNC connector.

pH Temperature Error Table												
°C	pH											
	2	3	4	5	6	7	8	9	10	11	12	
5	.30	.24	.18	.12	.06	0	.06	.12	.18	.24	.30	
15	.15	.12	.09	.06	.03	0	.03	.06	.09	.12	.15	
25	0	0	0	0	0	0	0	0	0	0	0	
35	.15	.12	.09	.06	.03	0	.03	.06	.09	.12	.15	
45	.30	.24	.18	.12	.06	0	.06	.12	.18	.24	.30	
55	.45	.36	.27	.18	.09	0	.09	.18	.27	.36	.45	
65	.60	.48	.36	.24	.12	0	.12	.24	.36	.48	.60	
75	.75	.60	.45	.30	.15	0	.15	.30	.45	.60	.75	
85	.90	.72	.54	.36	.18	0	.18	.36	.54	.72	.90	



Less than .1 pH Error Range



0 pH Error Range

#### Mounting Adapters:

For in-line applications, included will be the mounting adapter that fits into a standard 1/4" NPT tee, and the nut that secures the housing to the adapter.

For submersion applications, all that is required is a standard 1" NPTF threaded coupling and the appropriate length of 1" pipe. These parts are supplied by the user.

## 2.0 Installation

### General Guidelines

Note: After removing the electrode from the soaker bottle, be sure to remove the large o-ring from the electrode. This o-ring prevents soaker solution from leaking out of the bottle and is not part of the electrode.

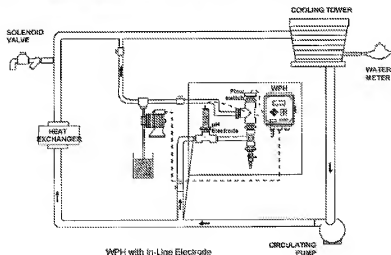
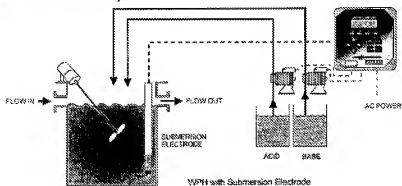
Instructions for mounting the electrode into the process solution will vary greatly with the type of electrode and the circumstances that are encountered in your application. Here are some general guidelines to assist you. Refer also to the typical installation drawings.

The electrode should be mounted such that the measuring surfaces will always stay wet. If the electrode dries out, it will respond slowly to changing pH/ORP values for 24 hours, and if dried out repeatedly, will fail prematurely.

For submersion applications, mount the electrode below the minimum solution level. If the tank will be completely drained, plan on removing the electrode and storing it in tap water (NOT DI water) or pH 4 buffer solution while the tank is empty. If this is undesirable, a recirculation loop may be installed and the electrode mounted in-line.

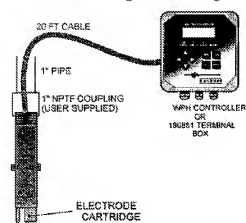
For in-line applications, where the electrode is installed in a pipe, the electrode should be placed on the discharge side of the pump (under positive pressure). A "U" trap should be installed so that if the flow stops, the electrode is still immersed in the solution. If the flow through the pipe can not be stopped to allow for cleaning and calibration of the electrode, then the electrode should be placed in a by-pass line with isolation valves to allow for electrode removal. Install the electrode vertically, with the measuring surface pointing down, at least 5 degrees above horizontal. (Refer to Installation drawings)

The electrode should be installed in an area where there is good solution movement and where it will respond rapidly to chemical additions. The placement of the electrode relative to the placement of chemical replenishment, along with the quality of the mixing, and the replenishment pump flow rate are all critical to accurate process control.

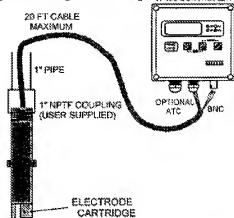


### Electrode Assembly

For submersion applications, attach the threaded end of the housing to a 1" NPTF coupling and appropriate length of 1" pipe. This should be sealed to prevent the solution from contacting the electrode housing cable. Remove the protective cap from the end of the electrode cartridge, and thread the cartridge into the housing until it is hand tight. The o-ring should seat against the housing.

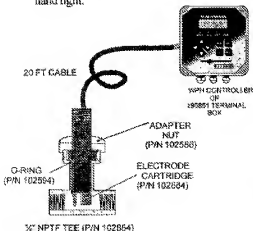


**ELECTRODE HOUSING WITH PREAMP  
SUBMERSION MOUNT**

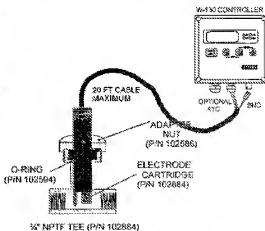


**ELECTRODE HOUSING WITHOUT PREAMP  
SUBMERSION MOUNT**

For in-line applications, feed the electrode housing cable through the adapter nut. Remove the protective cap from the end of the electrode cartridge, and thread the cartridge into the housing until it is hand tight. The o-ring should seat against the housing. Place the large o-ring into the mounting adapter groove, then place the electrode housing into the tee, and thread the adapter nut onto the tee until it is hand tight.



**ELECTRODE HOUSING WITH PREAMP  
IN-LINE MOUNT**



**ELECTRODE HOUSING WITHOUT PREAMP  
IN-LINE MOUNT**

### Wiring Instructions

For housings that contain the integral preamplifier, attach the 7-conductor cable directly to the controller:

Drain:	Earth Ground	
Orange:	VpH (pH +)	
Wht w/Orn stripe:	Com (pH -)	
Green:	TC + (optional)	TC = Temperature Compensation
Wht w/Grn stripe:	TC - (optional)	
Blue:	+ 5 VDC	
Wht w/Blu stripe:	- 5 VDC	

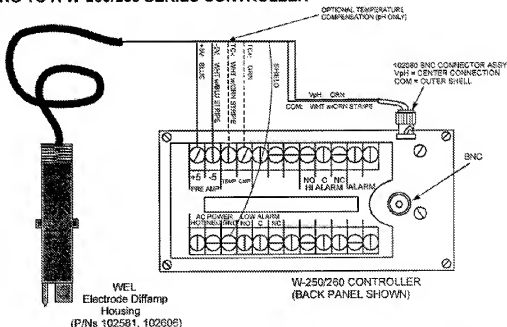
If the required cable length exceeds the 20 feet that is supplied, wire the housing to a 190851 terminal box, then use p/n 102535 cable to reach the instrument.

For housings that do not contain the integral preamplifier, attach the male BNC connector on the housing to the female BNC connector on the instrument, and the optional temperature wires to the temperature input terminal strip on the instrument:

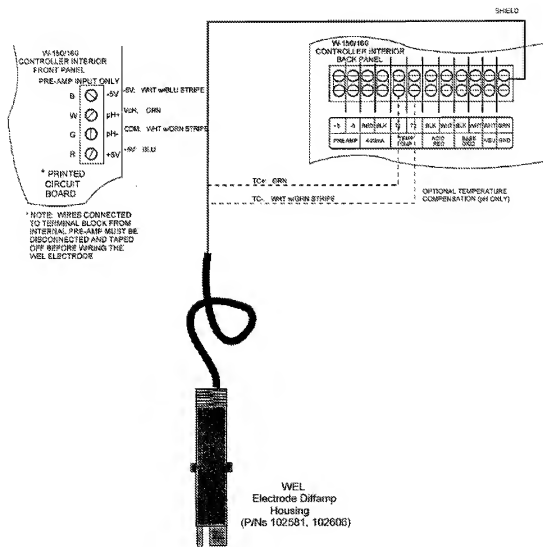
Grn:	Earth Ground
Red:	TC (polarity not critical for TC)
Blk:	TC (polarity not critical for TC)
	[TC = Temperature Compensation]

The non-amplified signal is extremely sensitive! Never cut, splice or otherwise harm the integrity of the coaxial cable or BNC connector! If the distance between electrode and instrument exceeds 20 feet, use the housing that contains a preamplifier, or purchase an externally mounted preamplifier.

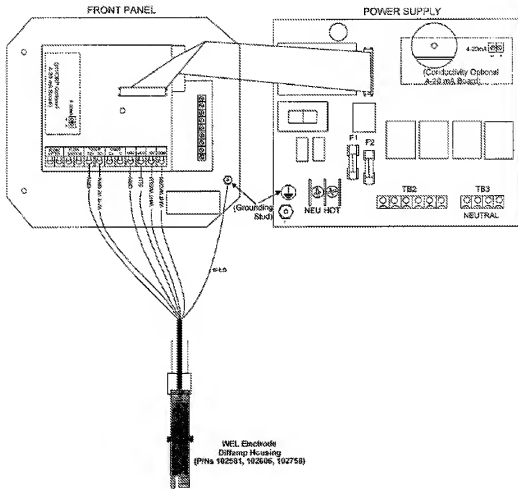
### ■ WIRING TO A W-250/260 SERIES CONTROLLER



■ WIRING TO A W-150/160 SERIES CONTROLLER

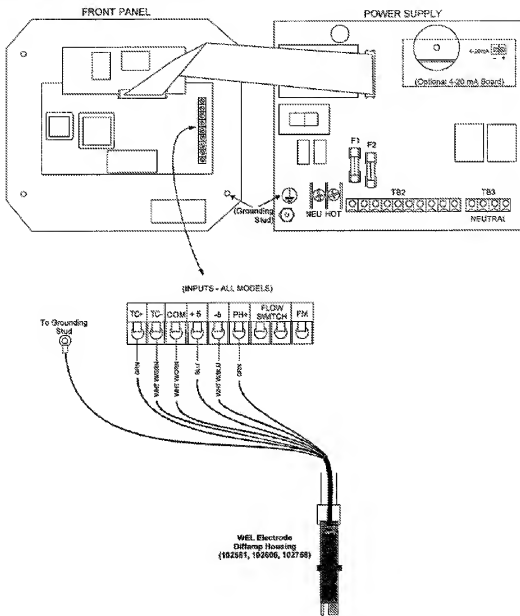


■ WIRING TO WNI/WDT310/WDP SERIES CONTROLLERS





■ WIRING TO A WPH300/WDP SERIES CONTROLLER



### 3.0 Maintenance

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The Combination pH/Reference Electrode or ORP (REDOX) Reference Electrode is ruggedly made and easy to use. Because the pH responsive glass bulb or flat surface is relatively thin, care should be taken so that the bulb does not become scratched or broken. It is also important that ORP measuring surfaces are not scratched or gouged. The suggestions in this sheet are intended to help avoid these problems.

The built-in sealed reference design of this electrode eliminates the need to add filling solutions and minimizes reference dryout. This design feature also allows the electrode to be used in pressurized systems (refer to specification sheets or consult the factory for maximum pressure/temperature limit information).

#### Important Considerations

1. The pH Electrode is shipped in a plastic bottle or cap containing a solution of 4 buffer and potassium chloride. ORP (REDOX) Electrodes are shipped in caps containing a piece of cotton wetted with tap water. The electrode should remain in the bottle or cap until it is used. If the electrode is used infrequently, the bottle or cap and its solution should be saved and the electrode stored in it.
2. Electrodes are a form of a battery and have limited shelf lives. Electrodes in inventory should be rotated so that older electrodes are used first.
3. Vigorous stirring brings a sample, buffer or rinse solution to the measuring surface more quickly and will improve speed of response. Care must be taken to keep the electrode's measuring surface from striking a surface and getting scratched or broken.
4. After exposure to a sample, buffer or rinse solution, carryover can be minimized by blotting - *never by wiping* - the electrode with a clean, non-abrasive paper or a clean cloth towel.
5. As a rinse solution, use a part of the next sample or buffer which is to be measured. This action also will minimize contamination from carryover.
6. When calibrating, use a buffer close in value to that expected from the sample for 1 point calibrations or as the first buffer for 2 point calibrations (see below). This action will minimize span errors.
7. Readings stabilize faster in some solutions than others; allow time for the reading to stabilize. In general, with new electrodes stable readings in buffers are obtained in 10-15 seconds.
8. All pH electrodes age with time. Aging is characterized by shortened span and slower speed of response. Aging is best detected by the 2 point calibration method. If the pH meter has manual or microprocessor slope (span) controls, the controls can be adjusted to compensate for electrode span errors (but will not affect the speed of the response).
9. Electrodes should be replaced when their readings cannot be corrected by the meter's controls and/or when their speed of response is too slow for the application for which they are being used. The frequency of electrode replacement is a function of the application; electrodes operating in hot liquids at very high or very low pH values will have shorter lives than those operating at neutral

pH and ambient temperature.

10. Coatings on an electrode's surface prevent new liquids from contacting an electrode's measuring surface and can mimic the effects of electrode aging. Before concluding that an electrode needs replacing, check the surface for coatings.

11. Temperature affects electrode readings in two ways. First, the output of an electrode varies with temperature. For pH electrodes this effect can be corrected by manual or automatic temperature compensation (ORP/REDOX readings are not correctable for the effect of temperature changes). Second, the real pH or ORP value, independent of the electrode measuring the value or the use of temperature compensation, is temperature dependent. This fact means, for example, that the readings at 25°C and 75°C will be (and, in fact are) different.

### **CALIBRATION**

As a rule, follow the procedure shown in the pH Meter's Instruction Manual. These procedures will vary depending on whether the meter is a simple type with manual adjustments, a micro-processor type or a pH transmitter.

### **FREQUENCY OF CALIBRATION**

The frequency of calibration is a function of many factors. These factors include:

1. The accuracy required by the application.
2. The value of the off-specification product versus the cost of calibration.
3. The coating or abrasive nature of the application.
4. The stability of the pH Electrode and pH Meter as a system.

The frequency of calibration is really determined by experience. At a new installation, calibration might initially be checked every few hours or shift with the calibration changes noted in a log. As a pattern of longer stability is found, the time between calibration checks can be increased to once a day or once a week. Although the frequency of calibration is solely the responsibility of the user, once a week is the longest recommended interval between calibrations.

### **SYSTEM CALIBRATION CONCEPTS**

The pH Electrode and the pH Meter should always be calibrated as a system. Electronic calibration of a pH Meter with a pH signal simulator checks the meter only and does not correct for imperfections of the pH Electrode. Even if perfect when new, the performance of pH electrodes varies with time, usually in an unpredictable way. When changing electrodes or connecting an electrode to a different pH meter, re-calibration must be performed.

### **SINGLE POINT CALIBRATIONS**

Single point calibrations involve the use of one pH buffer. They are the easiest to make but can provide misleading results. They should only be used for quick checking from time to time.

### **TWO POINT CALIBRATIONS**

As their name implies, 2 point calibrations use 2 pH buffers: for example, buffers 7.00 and 4.00 or buffers 7.00 and 10.00. Two point calibrations correct for the pH electrode's offset and span errors. Since both the offset and span vary with time, the 2 point method is the preferred one.

### **GRAB SAMPLE CALIBRATIONS**

The Grab Sample Calibration method is used when it is difficult or undesirable to remove an electrode from a system. This method involves obtaining a sample of the liquid being measured and noting the meter's reading at that time. The sample's reading is obtained by use of a calibrated lab or

portable meter and that reading is compared to that of the on-line meter. The on-line meter is adjusted by the difference between the readings. It is important to use the difference between the readings because the system's reading may have changed in the intervening time. It is important that the sample being measured by the lab meter be at the process temperature or erroneous results may occur (See #11 on the previous page).

#### **CALIBRATION PROCEDURES**

Stepwise calibration procedures are noted in the pH Meter's Instruction Manual. The following suggestions will help make calibrations as accurate as possible:

1. Before placing the electrode in a new buffer, use an absorbent paper towel or clean absorbent cloth to blot, not wipe, off any liquid that clings to the electrode. This action will minimize carry-over that could contaminate the buffer.
2. Always use fresh buffers. Safely dispose of the buffers after they have been used for calibration. Do not return them to their bottles; this action could contaminate the buffers.
3. Stir the electrode in the buffer to make certain that the fresh buffer quickly reaches the electrode's measuring surface.

#### **INTERMITTENT OPERATION**

Some facilities are only operated part of the time. When out of operation, electrodes must not be allowed to be exposed to air and become dry. Electrodes should be removed from such systems and stored in their bottles and caps or in a beaker, filled, preferably with 4 buffer. In some instances, power to the meter is shut off; this condition can be harmful to the electrodes. Electrodes should be disconnected from un-powered meters.

#### **ELECTRODE CLEANING**

Coating of an electrode's measuring surface can lead to erroneous readings including shortened span and slow response times. The type of coating determines the type of cleaning technique.

Soft coatings can be removed by vigorous stirring, by use of a squirt bottle, or very carefully, by gently wiping with a soft, clean non-abrasive paper or cloth.

Hard coatings should be chemically removed. The chemical used to remove the coating should be the least harsh chemical that dissolves the coating in 1 or 2 minutes and does not attack the electrode's materials of construction. For example, a calcium carbonate coating might be removed with 5% HCl (muriatic acid).

Oily or organic coatings are best removed with detergents or an appropriate solvent that does not attack the electrode's materials of construction. For example, isopropyl alcohol might be used but acetone should be avoided if the electrode's body is made of CPVC.

**Note:** When using chemicals or solvents, care should be taken and appropriate eye, face, hand, body and/or respiratory protection should be used.

Never abrade or sand a pH electrode's surface. However, the measuring surface of an ORP/REDOX electrode may be gently abraded by use of 600 grade wet silicon carbide paper, jewelers rouge or very fine steel wool.

## Notice

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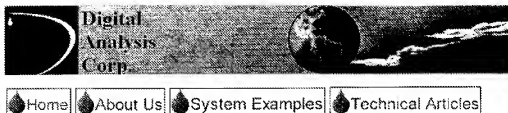
## Statement of Limited Warranty

*WALCHEM Corporation warrants equipment of its manufacture, and bearing its identification to be free from defects in workmanship and material for a period of 24 months for electronics and 12 months for mechanical parts and electrodes from date of delivery from the factory or authorized distributor under normal use and service and otherwise when such equipment is used in accordance with instructions furnished by WALCHEM Corporation and for the purposes disclosed in writing at the time of purchase, if any. WALCHEM Corporation's liability under this warranty shall be limited to replacement or repair, F.O.B. Holliston, MA U.S.A. of any defective equipment or part which, having been returned to WALCHEM Corporation, transportation charges prepaid, has been inspected and determined by WALCHEM Corporation to be defective. Replaceable elastomeric parts and glass components are expendable and are not covered by any warranty.*

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P/N 180109 H1  
Nov 2004

**WALCHEM**



## pH Probe Maintenance

The success or failure of pH measurement depends on the proper application of the probe and proper subsequent maintenance of the probe. The procedures described within apply to the most common pH probe in use today and that is the flat surface combination pH probe.

The most common failure mode associated with pH probes is breakage. The pH electrode is a very thin glass membrane that is easily damaged. Foreign object damage within the installation or mechanical shock during calibration are often the culprits. The next most common cause of failure is a plugged reference junction. The reference junction consists of a porous material, usually ceramic or Teflon, that must remain open. The junction creates a fluid interface between the reference material which is a liquid and the process fluid. A flow, albeit infinitesimally low, must exist from the reference electrode to the process fluid. In environments where there are high solids, oils or grease this junction can become plugged.

### Probe Cleaning

When the reference junction becomes plugged the probe will become sluggish and unresponsive. In many cases the junction can be cleaned with aggressive alkaline cleaners (for oil plugging) or dilute acids (for salt deposits) or a combination of both. In most cases, for probes with large junction surface areas the junction material can be scraped away with a screw driver revealing a new surface. Aggressive procedures are sometimes necessary to bring life back to a dead probe.

The glass pH sensing membrane may also require service in some applications. This membrane can become dehydrated or coated with a thin layer of deposits. The best procedure for cleaning or rehydrating the glass is to soak the probe in a pH buffer of 4.0 for several hours. If this does not work then immersing the probe in hot buffer 4.0 solution will usually work.





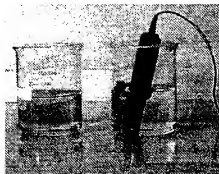
In most cases the aggressive procedures described are necessary. Cleaning can usually consist of simply rubbing the probe with a cloth or rag. Care must be taken not to scratch the glass membrane. The glass is thin and delicate but still requires aggressive cleaning with a cloth.

pH Probes will likely be the most service intensive part of the plant. Most measuring elements such as flow sensors, etc. rarely need service. However, pH probes, in general, require service as often as 2 or 3 times a day. If cleaned and calibrated once monthly will suffice.

Unlike flow sensors, temperature sensors, or just about any other type of sensor that we commonly use in industry, the pH electrode is relatively unstable and maintenance intensive. pH Probes will normally require weekly or monthly cleanings and monthly calibrations. The actual frequency is a function of the installation environment but could be as often as a couple of times a day.

pH Electrodes must be calibrated using a two point method with the appropriate buffer standards. There are some manufacturers that describe single point calibrations, however we cannot endorse this method. pH probe failure modes are numerous and can escape conventional single point checks. Therefore a two point calibration must be performed.

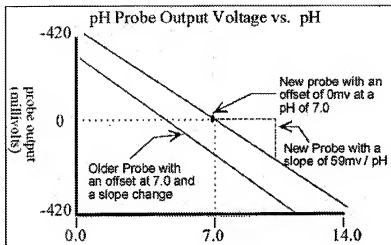
To perform a two point calibration two buffer solutions are required, as the method implies. These buffers should be based upon the normal measurement range that the probe operates in. An effluent monitoring probe or neutralization probe should use pH buffers 7.0 and 10.0. Likewise, a pH probe in a hexavalent chromium reduction system, for example, should be calibrated with a 2.0 (or 4.0) and a 7.0 buffer solution.



Care must be taken not to cross contaminate the buffers. As the name implies pH buffers solutions are designed to be buffering at their advertised pH value. They can, however, become easily contaminated which, of course, renders them useless. The procedures that follow on the next page indicate that the probe must be rinsed and wiped dry when moving from one buffer to the next. As one might expect it is easy to drag out buffer from one beaker to the next. Therefore rinsing the probe and wiping dry is essential when moving between buffer solutions. DI or demineralized water is not required to rinse the probes, any clean water source will suffice.

On another topic, for a moment, it is important to point out that DI or demineralized water should not

be used to store a probe. This will actually shorten probe life. A pH probe should be stored in a solution with high ionic strength, preferably a pH buffer solution of 4.0.



A new pH probe response of 59mv

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The procedure that follows allows for a complete calibration that tracks and adjusts changes to both the offset of a pH probe and the slope.

The actual calibration procedure will vary from device to device, but the actual function is almost identical for any of the instruments on the market today. Essentially the probe must be calibrated at a Zero point and at a Span Point. Typically a probe will be calibrated at a pH of 7.0 and 10.0. The 7.0 buffer solution is the Zero point calibration and the 10.0 buffer is used for the Span adjustment. The procedure that follows assumes that the transmitter is equipped with separate Zero and Span potentiometers.

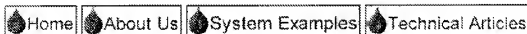
- 1) Removes the probe from service and clean as previously described. Inspect the probe for any obvious damage.
  - 2) Immerse the probe in a pH buffer solution of 7.0 and wait for the reading to stabilize. This may take as long as 2 minutes, although for a new probe this should occur within 30 seconds. Record the indicated pH value but do not calibrate.
  - 3) Rinse the probe with clean water and wipe dry. Immerse the probe in a 10.0 buffer solution and allow to stabilize as in step 2. Record as in step 2.
- [Note Steps 2 and 3 are performed so that the calibration stability of the probe can be tracked. It is important to know before you perform the calibration how far the probe has drifted since the last calibration.]
- 4) Rinse the probe with clean water and wipe dry. Immerse the probe in a pH buffer solution of 7.0 and wait for the reading to stabilize. Adjust the Zero pot so that the pH indicator reads 7.0.
  - 5) Rinse the probe with clean water and wipe dry. Immerse the probe in a pH buffer solution of 10.0 and wait for the reading to stabilize. Adjust the Span pot so that the pH indicator reads 10.0.
  - 6) Repeat Steps 4 & 5 until the probe indicates 7.0 and 10.0 in the respective buffer solutions.

Note: With older analog transmitters (as in the example above) the adjusting the Zero pot may have an



effect on the Span and visa versa. With newer microprocessor based devices the procedures are somewhat simpler in that there is no interaction between the two.

With newer Microprocessor based pH transmitters, such as those used on all of our systems, the procedures may be slightly different, however, the fundamentals remain the same. Refer to the Operations and Maintenance manuals for your system for specific calibration procedures.



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